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New Rearrangement in the Quinoline Series

By COLIN E. CRAWFORTH*

(Department of Chemistry and Biology, Harris College, Preston PR1 2TQ)

and O. METH-COHN

(Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT)

N-Lithio-1,2-dihydroquinolines (I) react with Summary acid chlorides or esters to give the corresponding Nacylated derivatives (II), certain of which undergo rearrangement to the tertiary carbinols (III), in the presence of organolithium compounds.

PREVIOUS assumptions that reactions between quinolines and organolithium reagents proceed through the N-lithio-1,2-dihydroquinoline intermediates (I) have recently¹ been given substantial support. Thus with ethyl chloroformate the 1,2-dihydroquinolines (II; $R^2 = OEt$) are formed.

quinoline and phenyl-lithium, presumably (Ia), was R = Ph)³ for this compound. treated with 1 equiv. of methyl benzoate or benzoyl chloride at $0^{\circ 2}$ the major product was (IIa) (75%)[†] to- or (Ia) in boiling ether solvent gave the carbinol (III) (60gether with a by-product (5%). This by-product was the 80%) together with n-butane or 2-phenyl-1,2-dihydroquinosole product (100% based on the ester) when 0.5 equiv. of line respectively. Structural analogies between (IIa) and methyl benzoate is added at refluxing ether temperatures. 'Reissert' compounds (II; $R^1 = CN$, $R^2 = aryl$), sub-



When the intermediate from the reaction between Analysis and spectral data indicate the structure (III;

Subsequent reactions between (II) and n-butyl-lithium,



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stantiated by similarities in their spectra,⁴ led us to believe that this reaction was analogous to the base-catalysed rearrangement^{4b} of such Reissert compounds to 2-aroylquinolines (Scheme). The interaction of methyl p-toluate and (Ia) gave the carbinol (III; R = p-tolyl) confirming that one aryl group came from the ester and the other from the aryl-lithium.

The acetyl derivatives (IIc and d), † and also (IIb) † [prepared from the adducts (I) and the corresponding methyl ester or acid chloride at 0°] failed to undergo rearrangement; instead attack at the amide grouping occurred to give amongst other products 2-phenyl- or 2-n-butyl-quinoline. The acetyl Reissert analogues behave in a similar manner.4e It is probable that in (IIb) the α -hydrogen is not sufficiently acidic to be removed by the organolithium base. Hence for successful rearrangement of the (II) to the tertiary carbinols (III), it appears that both R^1 and R^2 in (II) must be aryl.

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† Satisfactory spectra and analytical data were obtained for these compounds.

¹ C. E. Crawforth, O. Meth-Cohn, and C. A. Russell, J.C.S. Chem. Comm., 1972, 259.
² For the pyridine analogues, see C. S. Giam and E. E. Knaus, Tetrahedron Letters, 1971, 4961.
³ M. R. F. Ashworth, R. P. Daffen, and D. Ll. Hammick, J. Chem. Soc., 1939, 809.
⁴ (a) R. Bramley and M. D. Johnson, J. Chem. Soc., 1965, 1372; (b) V. Boekelheide and J. Weinstock, J. Amer. Chem. Soc., 1952, 74, 660; (c) W. E. McEwan, R. H. Terss, and I. W. Elliot, *ibid.*, p. 3605; (d) R. F. Collins and T. Henshall, *ibid.*, 1958, 80, 159; (e) A. P. Wolf W. E. McEwan, and R. H. Glazier *ibid.* 1956, 78, 861. Wolf, W. E. McEwan, and R. H. Glazier, ibid., 1956, 78, 861.